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Neutron Powder Diffraction Study of the Nuclear and Magnetic Structures of the Oxygen-Deficient Perovskite $YBaCuCoO_5$

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The nuclear and magnetic structures of the oxygen-deficient perovskite $YBaCuCoO_5$ have been determined by neutron powder diffraction at room temperature. The nuclear structure has the symmetry of space group $P4/mmm$ and lattice parameters a = 3.8679(1), c = 7.5674(2) Å. Copper and cobalt atoms are completely disordered in this compound and the oxygen vacancies are located on the layer of the yttrium atoms. As a consequence of this configuration, the Co/Cu atoms have fivefold, pyramidal coordination. The pyramids share corners in the $(Co/Cu)O_2$ planes, as well as in the direction of the c axis, thus forming slices of two pyramids with opposite orientation separated by layers of yttrium atoms. The Ba atoms, on the other hand, have 12-fold coordination as in nondefective perovskites, and the Y atoms have eightfold prismatic coordination as in the superconductor $YBa_2Cu_3O_{6+\delta}$. The magnetic structure is based on a unit cell related to that of the nuclear structure by an axis transformation of matrix (1, −1, 0/1, 1, 0/0, 0, 2). The magnetic origin of the extra reflections observed experimentally was established by polarized neutron diffraction measurements. The reflection conditions of the magnetic intensities are consistent with a model in which magnetic moments of equal modulus have alternately ferromagnetic and antiferromagnetic orientations along the c axis and antiferromagnetic ordering in the planes perpendicular to c. If we also assume that the magnetic structure has tetragonal symmetry, then the magnetic moments have to assume an orientation parallel to the c axis of the unit cell.

INTRODUCTION

The study of oxygen-deficient perovskites has recently received attention because of the close chemical and structural relationship between these materials and the superconducting, perovskite-related copper oxides. In particular, the removal of oxygen and the effect of the coordination and distribution of solid solute atoms on the ordering of oxygen vacancies in the substitution compounds derived from the "123" superconductor can be best understood from a study of structurally similar defective perovskites.

The ordering of oxygen vacancies has been determined by X-ray single-crystal and/or neutron powder diffraction in several oxygen-deficient perovskites of formula ABO_{3-x}, ($x \approx 0.5$) (1–4). The structural diversity in these compounds has recently been analyzed by Vaughey and Poeppelmeier (5) who have pointed out that, when the fraction of anion vacancies is large (~17%), the vacancies adopt an ordered arrangement which is largely determined by the coordination requirements of the A and B atoms. Thus, in $LaSrCuAlO_5$ (2), the oxygen atoms of the AlO layers assume a configuration which results in tetrahedral coordination of the aluminum atoms similar to that found for Al and Co in $YSr_2Cu_2AlO_7$ (6) and $YSr_2Cu_2CoO_7$ (7), respectively. On the other hand, in the structure of $YBaCuFeO_5$ (1, 5), the oxygen vacancies are localized on the plane of the yttrium atoms as is, in part, the case for the "123" superconductor $YBa_2Cu_3O_{6+\delta}$. As a consequence of this structural feature common to the two compounds, the Cu and Fe atoms of $YBaCuFeO_5$ have pyramidal fivefold coordination similar to that of the plane copper atoms in $YBa_2Cu_3O_{6+\delta}$.

Magnetic susceptibility measurements have shown that magnetic ordering is present in both $YBaCuFeO_5$ and $Ca_2Mn_2O_5$ below 460 and 350 K, respectively (1, 4). Antiferromagnetic order in $YBaCuFeO_5$ was corroborated by Mössbauer spectroscopy (8). To this point, however, the magnetic structure of both compounds has not been determined, as the neutron powder diffraction data were collected in the paramagnetic domain in the case of $YBaCuFeO_5$ (1), and the diffraction lines of magnetic origin were excluded from the refinements of the nuclear structure in the case of $Ca_2Mn_2O_5$ (4).

The oxygen-deficient perovskite $YBaCuCoO_5$ was prepared as part of an ongoing study of substitution compounds related to the "123" superconductor. Neutron powder diffraction data were collected in order to determine the nuclear and magnetic structures of this material, and to examine its structural relationship to $YSr_2Cu_2CoO_7$ (7). The results of this work are reported herein.

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TABLE 1
Collection of Intensity Data

Monochromatic beam	220 reflection of a Cu monochromator
Wavelength	1.545(1) Å
Horizontal divergences	10′, 20′, 10′ of arc for the in-pile, monochromatic beam, and diffracted beam collimators, respectively
Sample container	Vanadium can of about 10 mm diameter
2θ angular range	5–120°, steps: 0.05°
Scattering amplitudes (10^{-12} cm)	b(Y) = 0.775, b(Ba) = 0.525, b(Cu) = 0.772, b(Co) = 0.253, b(O) = 0.581

Note. Measurements made at room temperature; for polarized neutron beam experiments and temperature dependence, see text.

EXPERIMENTAL AND RESULTS

(*a*) *Sample Preparation*

The sample of $YBaCuCoO_5$ used in the experiment was prepared from liquid-mixed citrate precursors. Reagent grade Y_2O_3, $BaCO_3$, and $CuCO_3 \cdot Cu(OH)_2 \cdot 0.5H_2O$ were dissolved in boiling citric acid, and $CoC_2O_4 \cdot 4H_2O$ dissolved in hot concentrated HNO_3 was added to this solution. The clear citrate gel was then dehydrated at 180°C and the resulting product was finely milled and incinerated in air at 450°C. The powder thus obtained was pressed into pellets which were placed in a corundum boat over a protective layer of powder having the composition of the master sample. The pellets were then fired four times for 60 hr at 950°C in an atmosphere of purified oxygen and rehomogenized after each firing. The last firing cycle was followed by 30 hr of annealing at 370°C in the same oxygen atmosphere. The single phase character of the product was verified by high-resolution powder X-ray diffraction with a Guinier–Hägg camera using Cu$K\alpha_1$ radiation and Si as an internal standard. The threshold sensitivity estimate for detecting a second phase in this system was ~0.5%. The lattice parameters determined in this experiment were: a = 3.8701(5) Å and c = 7.5602(14) Å at 298 K.

The oxygen content corresponds to the formula $YBaCuCoO_{4.98(1)}$ and was determined iodometrically by dissolving a finely milled solid sample in 1 *M* HCl with KI under inert Ar atmosphere, and by titrating the released iodine.

(*b*) *Neutron Powder Diffraction*

Neutron powder diffraction measurements were made with the high resolution five-counter diffractometer at the Reactor of the National Institute of Standards and Technology, using the experimental conditions indicated in Table 1. The refinements were carried out with the Rietveld method (9) adapted to the multicounter geometry and modified to include background parameters (10). In these calculations, the peak shape was described by a Pearson function.

The first refinements based on neutron powder intensity data were made using a model of initial atomic parameters similar to those obtained for $YBaCuFeO_5$ (1). The assumed symmetry was that of space group *P*4*mm*, which allows two crystallographically distinct sites for cobalt and copper. This first set of calculations resulted in acceptable values of the R factors (R_N = 4.91, R_p = 6.88, R_w = 9.80, R_E = 6.63 χ = 1.48) and indicated a disordered distribution of the cobalt and copper atoms over the positions 1*b* (the occupancies for positions at $\frac{1}{2}$, $\frac{1}{2}$, 0.28 were 0.47(7) and 0.53(7) for Cu and Co, respectively, and those for positions $\frac{1}{2}$, $\frac{1}{2}$, 0.72 were 0.53(7) and 0.47(7), respectively). However, the standard deviations on the atomic positional parameters were unusually high (~3 units in the third decimal figure) and the z coordinates and thermal factors of Cu and Co atoms on the two sites 1*b*, as well as those of the oxygen atoms on the sites 2*c*, showed correlation factors as high as 98%, indicating that the symmetry of the structure is higher than *P*4*mm*.

Moreover, some fairly strong reflections, mainly in the low 2θ region of the powder pattern ($2\theta \approx 17.5°$, 24.2°, and 37.5°), could not be accounted for by the adopted model, but could be indexed in terms of a unit cell of parameters $a_M = b_M = a_N\sqrt{2}$, $c_M = 2c_N$, i.e., related to the parameters a_N, b_N, c_N determined from the X-ray diffraction patterns by the transformation (1, −1, 0/1, 1, 0/0, 0, 2). Since the extra reflections are not present in the X-ray diagrams and are confined to low 2θ values, they were attributed to magnetic ordering of the structure.

In order to establish unambiguously the magnetic origin of the low angle reflections, we made polarized neutron diffraction measurements. This technique determines the cross section between neutron spin states (11). The polarizing analyzer and monochromator both reflect only (+) state neutrons, thus one can immediately measure the

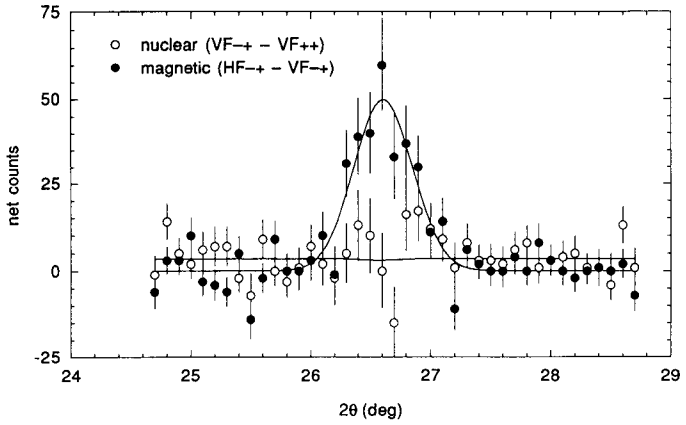

FIG. 1. Compilation of polarized beam diffraction pattern around the 011 reflection of $YBaCuCoO_5$. The closed symbols (●) are the difference between the horizontal and vertical field spin flip cross sections, which gives the magnetic component of the reflection. The open symbols (○) are the difference between the vertical field spin flip and nonspin flip cross sections, which is the coherent nuclear Bragg component of the reflection. The 011 reflection is purely magnetic, with no nuclear structure contribution.

nonspin flip cross section in the (+ +) scattering geometry. The spin flip cross section can be measured in the (− +) scattering geometry, where a π flipper (a device which momentarily applies a perpendicular magnetic field to the neutron, causing it to undergo Larmor precession by π radians) is used to flip the neutrons reflected off the monochromator to the (−) spin state. These (−) state neutrons impinge on the sample, and are ultimately detected only if they undergo a spin flip scattering process, since the analyzer will only reflect (+) state neutrons to the detector.

Coherent nuclear Bragg scattering is always a nonspin flip process. On the other hand, the magnetic Bragg cross sections depend on the geometrical relationship between the neutron polarization **P** and the scattering vector τ. In the case where $\mathbf{P} \parallel \tau$, the magnetic cross section is purely spin flip, whereas in the case where $\mathbf{P} \perp \tau$, the magnetic cross section is divided equally between the (− +) and (+ +) cross sections. A purely magnetic reflection, therefore, can be identified when $\mathbf{P} \parallel \tau$, through the observation of the reflection in the (− +) cross section, and the lack of the reflection in the (+ +) geometry. Alternatively, if there is overlap of structural and magnetic reflections, the two can be separated by taking the appropriate difference between diffraction patterns. The difference between the (+ +) and (− +) cross sections in the vertical field case, where $\mathbf{P} \perp \tau$, eliminates the magnetic scattering and leaves the coherent nuclear Bragg scattering. Subtracting the $\mathbf{P} \perp \tau$ (− +) cross section from the $\mathbf{P} \parallel \tau$ (− +) cross section results in only the magnetic scattering cross section.

The data necessary for this measurement were collected on the BT-2 triple-axis polarized beam spectrometer. Heusler alloy (Cu_2MnAl) crystals in reflection geometry were used as polarizing monochromator and analyzer. Neutrons of wavelength of $\lambda = 2.35$ Å were used, together with a graphite filter to suppress higher-order wavelength contamination, and collimations of 60′-60′-Sample-60′. There was no collimation between analyzer and detector. In this configuration, the instrumental flipping ratio was ≈ 10.

Diffraction scans across the position of the 011 reflection were performed, taking data for all four cross sections: horizontal field (+ +) and (− +), and vertical field (+ +) and (− +). Figure 1 shows the appropriate difference patterns, formed as described above, showing the magnetic nature of the reflection. There is no nuclear Bragg reflection, only a magnetic Bragg reflection at the 011 location. This unambiguously demonstrates the presence of antiferromagnetic ordering in $YBaCuCoO_5$.

The temperature dependence of the intensity of the 011 peak was measured on a diffractometer with 10′-20′-10′ collimation (see Fig. 2), with the sample kept under vacuum. If the magnetic structure is collinear and the moments on each site are equal (vide infra), the intensity is proportional to $\langle \mu_z \rangle^2$, the square of the average value of the ordered moment. The solid curve through the data points is a fit obtained using a simple mean-field model for the temperature dependence of the sublattice magnetization. This model specifies that the only interaction between otherwise free magnetic ions is the effective field due to neighboring magnetic ions. In the case of an antiferromagnet, the reduced spontaneous sublattice magnetization σ is described (12) by a Brillouin function, dependent on the angular momentum and the ordering temperature, T_N. The intensity data were fitted to the square of the magnetization allowing the moment, the ordering temperature and a scale factor, which is proportional to $\langle \mu_z \rangle^2$ at

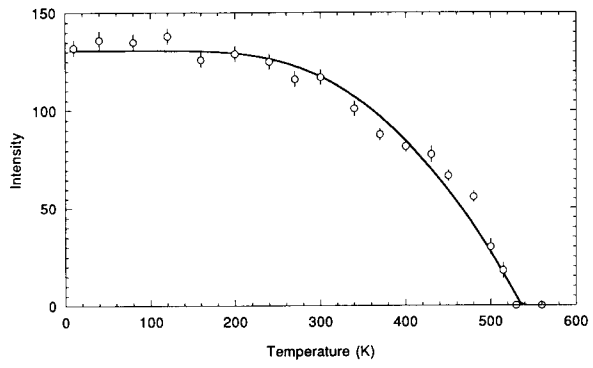

FIG. 2. Intensity of the 011 reflection of $YBaCuCoO_5$ as a function of temperature. The solid line is a fit to a simple mean-field model. The value of T_N obtained from the fit is $T_N = 536(3)$ K.

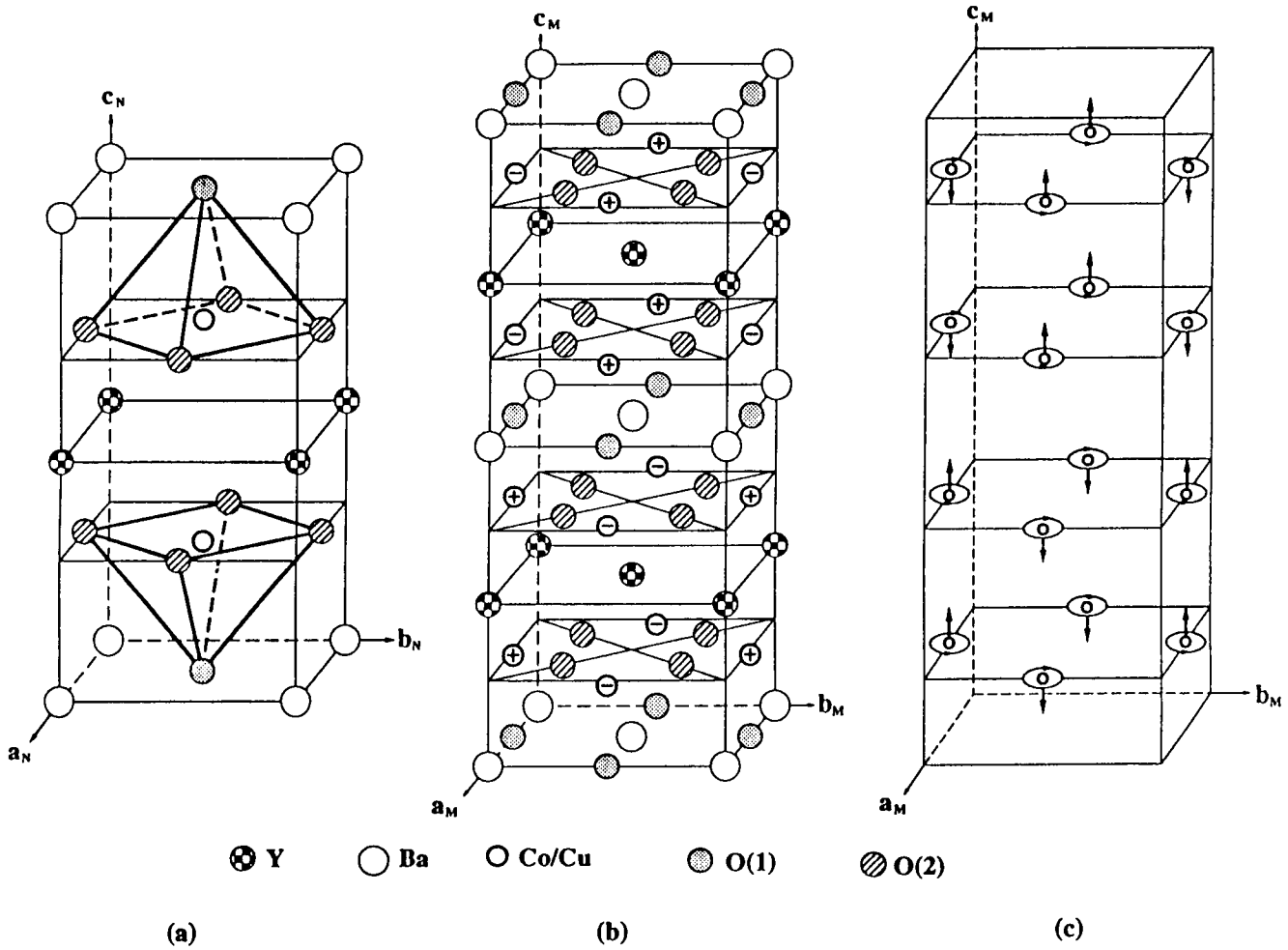

FIG. 3. (a) Nuclear structure of $YBaCuCoO_5$ showing the pyramidal coordination of the Co/Cu atoms. (b) Magnetic structure based on a unit cell of parameters $a_M = b_M = a_N\sqrt{2}$ and $c_M = 2c_N$. (c) Spin orientation assuming tetragonal symmetry for the magnetic structure.

$T = 0$, to be free parameters. The ordering temperature ($T_N = 536(3)$ K) and saturation moment thus established are quantitatively correct, as they are independently determined by the disappearance of the magnetic Bragg intensity and the full profile refinement, respectively.

As mentioned before, all reflections in the neutron powder pattern can be indexed in terms of a unit cell $\mathbf{a}_M$, $\mathbf{b}_M$, $\mathbf{c}_M$ related to the nuclear axes $\mathbf{a}_N$, $\mathbf{b}_N$, $\mathbf{c}_N$ by the transformation

$$\mathbf{a}_M = \mathbf{a}_N - \mathbf{b}_N, \quad \mathbf{b}_M = \mathbf{a}_N + \mathbf{b}_N, \quad \mathbf{c}_M = 2\mathbf{c}_N.$$

The observed condition for nonextinction, holding for all reflections, is $h_M + k_M + l_M = 2n$, indicating that the lattice is body centered. In addition, the observed magnetic reflections h'_M, k'_M, l'_M, obey the extra condition $l'_M = 2n + 1$ (and therefore $h'_M + k'_M = 2n + 1$), which indicates that magnetic and nuclear Bragg peaks are distinct. These observations are consistent with a model in which magnetic moments of equal moduli have alternately ferromagnetic and antiferromagnetic orientations along the c axis of the structure, and antiferromagnetic ordering in the planes perpendicular to this axis (Fig. 3).

As mentioned previously, the nuclear structure of $YBaCuCoO_5$ may be described as tetragonal, with a unit cell of axes $\mathbf{a}_N$, $\mathbf{b}_N$, $\mathbf{c}_N$, and with the Co and Cu atoms completely disordered over the positions $2h$ of space group $P4/mmm$. However, the symmetry of the whole structure (nuclear and magnetic) may be tetragonal or lower than tetragonal, depending on the magnitude and orientation of the magnetic moments with respect to the axes of the unit cell. Good agreement between observed and calculated intensities was obtained by adopting for the magnetic structure the symmetry of the Shubnikov space group $I4'/m'm'm$ (No. 536) (13). Refinements of this model were carried out using the magnetic form factors of Co and Cu given by Watson and Freeman (14) and Akimitsu and Ito (15) and constraining the magnitudes of the

TABLE 2
Refined Structural Parameters of $YBaCuCoO_5$ at Room Temperature

Atom		Position	x	y	z	B (Å^2)	Occupancy
Ba	1*a*	4/*mmm*	0	0	0	0.84(5)	1
Y	1*b*	4/*mmm*	0	0	$\frac{1}{2}$	0.54(3)	1
Cu	2*h*	4*mm*	$\frac{1}{2}$	$\frac{1}{2}$	0.2763(2)	0.74(4)	1
Co	2*h*	4*mm*	$\frac{1}{2}$	$\frac{1}{2}$	0.2763(2)	0.74(4)	1
O(1)	1*c*	4/*mmm*	$\frac{1}{2}$	$\frac{1}{2}$	0	1.24(5)	1
O(2)	4*i*	2*mm*	$\frac{1}{2}$	0	0.3140(1)	0.70(3)	4

Note. Space group: *P4/mmm*, a = 3.8679(1) Å, c = 7.5674(2) Å, V = 113.21(1) Å^3. Magnetic cell: a_M = b_M = 5.4700(1) Å, c_M = 15.1347(3) Å. The spin direction of the magnetic structure model used in the refinement: Shubnikov space group *I4'/m'm'm* (No. 536), $\mu_x = \mu_y = 0$, μ_z = 1.49(2) μ_B. The average magnetic moment of Co and Cu is 1.49(2) μ_B. R_{NM} = 5.77, R_p = 6.34, R_w = 8.08, R_E = 6.64, χ = 1.22, R_N = 5.26, R_M = 21.71.

magnetic moments of inequivalent atoms to be equal. Table 2 lists the results of these calculations and Fig. 4 shows the experimental and calculated profiles for the five counters of the diffractometer. Relevant interatomic distances and angles are given in Table 3.

DISCUSSION

The nuclear and magnetic structures of $YBaCuCoO_5$ are schematically illustrated in Fig. 3. This compound is virtually isostructural with $YBaCuFeO_5$ and is closely related to the "123" superconductor as indicated by the schemes:

$$\ldots[(BaO)_c(TO_2)_o(Y)_c(TO_2)_o(BaO)_c(TO_\delta)_o](BaO)_c(TO_2)_o(Y)_c\ldots \quad YBa_2Cu_3O_{6+\delta}$$

$$\ldots.[(BaO)_c(TO_2)_o(Y)_c(TO_2)_o](BaO)_c(TO_2)_o(Y)_c\ldots \quad YBaCuCoO_5$$

In the above sequences, T represents Cu in $YBa_2Cu_3O_{6+\delta}$, 50% Cu + 50% Co in $YBaCuCoO_5$, and either an ordered (5, 8) or an almost completely disordered distribution (1) of copper and iron atoms in $YBaCuFeO_5$. The subscripts o and c indicate whether the metal atoms are at the origin or at the center of the mesh in each layer, and the square brackets include the content of one unit cell of the structure (16). As mentioned previously, the sequence (BaO) (TO_2) (Y) (TO_2) (BaO) is present in all three compounds and, as a consequence, the yttrium atoms have eightfold prismatic coordination in the three structures, with similar Y–O distances (2.392 Å in $YBaCuCoO_5$, and average distances of 2.414 and 2.398 Å in $YBaCuFeO_5$ and $YBa_2Cu_3O_7$, respectively (17)). For the same reasons, the T atoms have similar fivefold pyramidal coordination in each compound, with somewhat different T–O distances. (These are 1.955 and 2.091 Å for the in-plane and apical distances in $YBaCuCoO_5$. For $YBaCuFeO_5$ the corresponding values are 1.999 and 1.998 Å for one of the two inequivalent pyramids and 1.966 and 2.130 Å for the other. For $YBa_2Cu_3O_7$, the average in-plane Cu–O distance is 1.945 Å and the apical one 2.295 Å). The Ba atoms, on the other hand, have 12-fold distorted cuboctahedral coordination in $YBaCuCoO_5$ (with Ba–O distances ranging from 2.735 to 3.064 Å), and coordination between 10- and 8-fold in $YBa_2Cu_3O_{6+\delta}$, due to the presence of the (CuO_δ) layer in this compound (Ba–O distances 2.741–2.946 Å).

The pyramids surrounding the T atoms share corners both in the TO_2 planes and along the direction of the c axis, thus forming slices containing two pyramids with opposite orientation, separated by layers of yttrium atoms. This feature, common to the Co and Fe compounds, is not present in the configuration of the "123" superconductor where the apical oxygen of the pyramids is part of the square-planar coordination of the chain copper atoms located on the layers (CuO_δ). The Co/Cu atoms are displaced from the plane of the O(2) oxygen atoms

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) of $YBaCuCoO_5$

Y–O(2)	×8	2.3920(5)
Ba–O(1)	×4	2.7350(1)
Ba–O(2)	×8	3.0636(6)
Cu/Co–O(1)		2.091(2)
Cu/Co–O(2)	×4	1.9549(3)
O(1)–O(2)		3.0636(6)
O(2)–O(2)		2.7350(1)
O(1)–Cu/Co–O(2)		98.39(5)
O(2)–Cu/Co–O(2)		88.78(2)
O(2)–Cu/Co–O(2)		163.22(11)

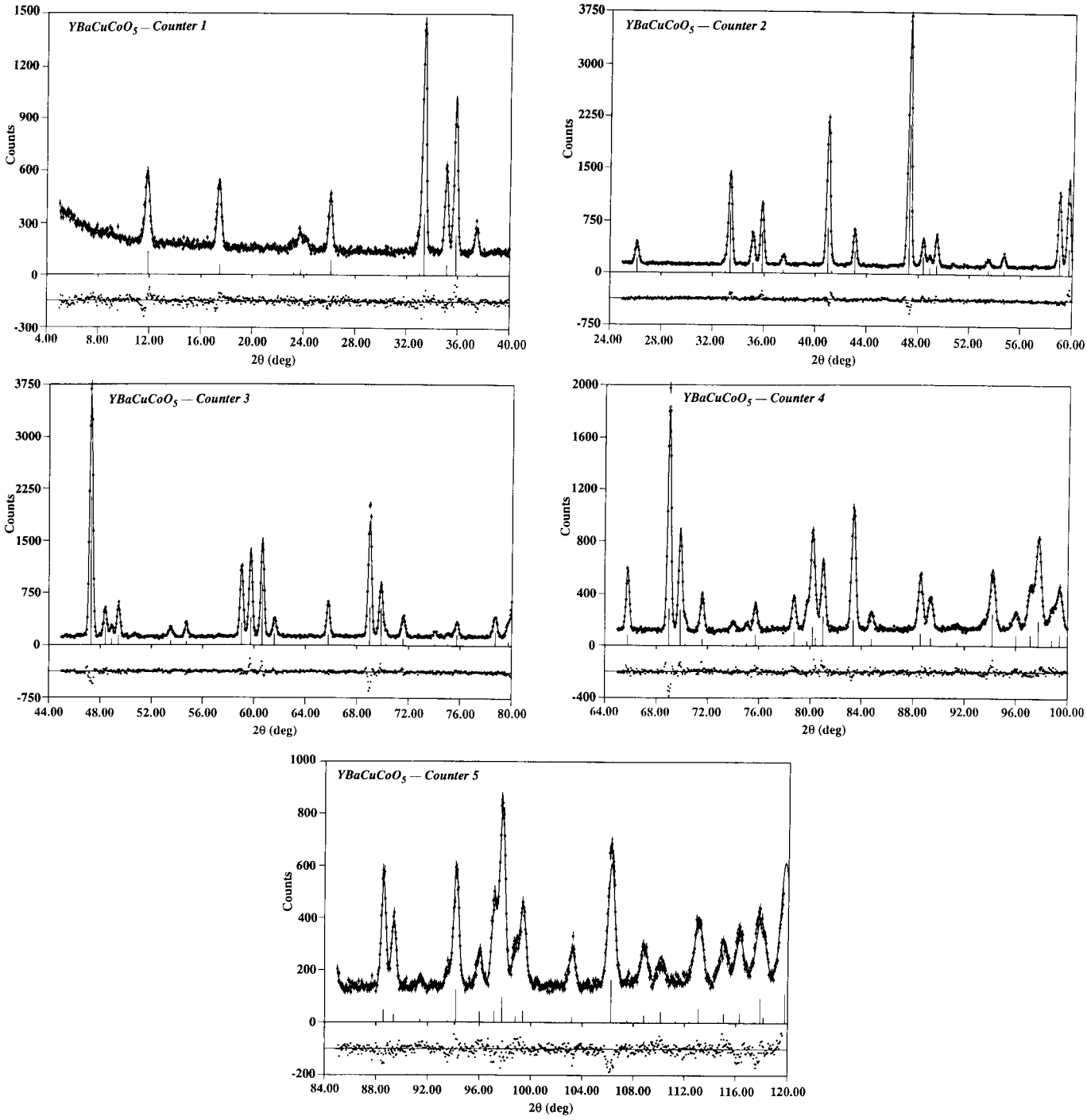

FIG. 4. Profile fit and difference plots for the neutron powder diffraction pattern of $YBaCuCoO_5$.

towards the center of the pyramids of about 0.28 Å. This value agrees well with the shift found for the plane-copper atoms in the "123" superconductor (0.28 Å) (18). The values found for the two Cu/Fe sites in $YBaCuFeO_5$ are 0.46 and 0.28 Å, indicating that the ordering of the Cu and Fe atoms in this structure may be more extensive than has been reported in the neutron diffraction study of Ref. (1).

A comparison of the structures of $YBaCuCoO_5$ and $YSr_2Cu_2CoO_7$ (7) shows that in the first compound Co and Cu atoms are disordered and in fivefold pyramidal coordination, while in the second Co substitutes exclu-

sively for the chain copper atoms and has tetrahedral coordination. A possible explanation for the different ordering of the oxygen atoms in the two structures can be found in the different size of the cations. Barium has a large radius and requires a high coordination number, keeping the configuration of the oxygen atoms around it as close as possible to that present in perovskite. Strontium, on the other hand, is smaller than Ba and assumes a ninefold coordination in $YSr_2Cu_2CoO_7$, leaving sufficient room for the oxygen atoms to adopt a tetrahedral configuration around Co.

The spin orientation in $YBaCuCoO_5$, represented in Fig. 3c, is based on the assumption that the magnetic unit cell remains tetragonal. In this system the magnetic atoms are located on special positions with site symmetry $2mm$, and consequently, the magnetic moments can only be oriented up or down along the c axis. Although this spin configuration is corroborated by acceptable agreement between observed and calculated magnetic intensities, the paucity of the magnetic diffraction data makes it impossible to exclude the existence of other models of symmetry lower than tetragonal, giving comparable agreement factors.

In conclusion, a new oxygen-deficient perovskite of formula $YBaCuCoO_5$ has been prepared and characterized structurally and magnetically. The oxygen vacancies have been found to be ordered with the same configuration present in $YBaCuFeO_5$ and on the yttrium layer of $YBa_2Cu_3O_{6+\delta}$. More determinations of magnetic structures, however, are necessary to draw conclusions about the kind of magnetic ordering possible in this class of materials.

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